PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-243463
(43)Date of publication of application : 08.09.2000

(51)Int.Cl. H01M 14/00
H01L 31/04

(21)Application number : 11-041299
(22)Date of filing : 19.02.1999

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(54) OPTICAL SEMICONDUCTOR ELECTRODEPHOTOELECTRIC CONVERTER AND PHOTOELECTRIC CONVERSION METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To efficiently utilize sunlight by providing a photoelectric conversion layer of one kind or more of a tetracyanoanthraquinodimetan compound and a perylene compound on the surface of a metal oxide semiconductor.
SOLUTION: This tetracyanoanthraquinodimetan compound is shown in a formula I. In the formula IR1 and R2 are a hydrogen atomalkyl grouparyl grouparalkyl groupalkoxyalkyl group or acyl group; n is 0 or 1. This perylene compound is shown in a formula II. In the formula IIR3 and R4 are a group represented by a formula IIIetc.; when the R3 and R4 are a group represented by the formula III1 is 0. In the formula IIIR5 and R6 are an aliphatic grouparomatic group or heterocyclic group; these may be substituted by a substituent. A1 represents a bivalent aliphatic grouparomatic group or heterocyclic group; these may be substituted by a substituent.

CLAIMS

[Claim(s)]
[Claim 1]An optical semiconductor electrode having a photoelectric

conversion layer by at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I) on the surface of a metal oxide semiconductor.
General formula (I)
[Formula 1]

In said general formula (I)R^1 and R^2It may be mutually the sameand may differa hydrogen atoman alkyl groupan aryl groupan aralkyl groupan alkoxyalkyl groupor an acyl group may be expressedand these may form the annular group of the following structure mutually. n expresses 0 or 1.
[Formula 2]

General formula (II)
[Formula 3]

In said general formula (II)R^3 and R^4Expressing the basis expressed with either following general formula (III) - (IX)these may be mutually the sameit may differ and at least one side expresses the basis expressed with either following general formula (III) - (VII) and (IX). l expresses 0-12when it is a basis which expresses 0 when R^3 and R^4 are the bases expressed with either following general formula (III) - (VIII)and is expressed with following general formula (IX).
General formula (III)
[Formula 4]

In said general formula (III)R^5 and R^6 may be mutually the sameit may differan aliphatic groupan aromatic groupor a heterocycle group is expressedand these may be replaced by the substituent. A^1 expresses a divalent aliphatic grouparomatic groupor heterocycle groupand these may be replaced by the substituent.
General formula (IV)
[Formula 5]

In said general formula (IV)A^2 expresses a divalent aliphatic grouparomatic groupor heterocycle groupand these may be replaced by the

substituent. R^7 and R^8 may be mutually the sameand it may differA hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-20-$(CH_2)_pCOOR^{18}$-$(CH_2)_pSO_3R^{19}$or $-(CH_2)_pNR^{20}R^{21}$ is expressed. $R^{18}R^{19}R^{20}$and R^{21} express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.
General formula (V)
[Formula 6]

In said general formula (V)A^3 expresses a single bond or a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by the substituent. R^9 expresses an aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by the substituent. R^{10} A hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-20- (CH_2) Express $_pCOOR^{18}$-$(CH_2)_pSO_3R^{19}$or $-(CH_2)_pNR^{20}R^{21}$. $R^{18}R^{19}R^{20}$and R^{21} express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.
General formula (VI)
[Formula 7]

In said general formula (VI)A^4 expresses a divalent aliphatic grouparomatic groupor heterocycle groupand these may be replaced by the substituent. X expresses an oxygen atoma sulfur atomor $>NR^{22}$. R^{11} and R^{12} A hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-20-(CH_2) Express $_pCOOR^{18}$-$(CH_2)_pSO_3R^{19}$or $-(CH_2)_pNR^{20}R^{21}$. $R^{18}R^{19}R^{20}R^{21}$and R^{22} express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.
General formula (VII)
[Formula 8]

In said general formula (VII)A^5 expresses a single bond or a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by the substituent. R^{13} expresses a divalent aliphatic grouparomatic groupor heterocycle groupand these may be replaced by the substituent. R^{14} A hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-20- (CH_2) Express $_pCOOR^{18}$-$(CH_2)_pSO_3R^{19}$or $-(CH_2)_pNR^{20}R^{21}$. $R^{18}R^{19}R^{20}$and R^{21} express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.
General formula (VIII)

[Formula 9]

In said general formula (VIII)A^6 expresses a divalent aliphatic grouparomatic groupor heterocycle groupand these may be replaced by the substituent. Y expresses -COOH-SOOHor $-NH_2$.
General formula (IX)
[Formula 10]

In said general formula (IX)X expresses two hydrogen atoms or MgZnFeConickelCuRuSnSnOTiOVOaluminum (OH)Ga (OH)or In (OH). $R^{15}R^{16}$and R^{17} express a hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-12-$(CH_2)_m$COOHor -$(CH_2)_m NH_2$. m and n express the integer of 0-12.
[Claim 2]The optical semiconductor electrode according to claim 1 whose tetracyano anthra quinodimethane compound expressed with said general formula (I) is a tetracyano anthra quinodimethane compound expressed with a following general formula (I-a).
A general formula (I-a)
[Formula 11]

In said general formula (I-a)Me expresses a methyl group. n expresses 0 or 1.
[Claim 3]The optical semiconductor electrode according to claim 1 or 2 whose metal oxide semiconductor is at least one sort chosen from titanium oxidetin oxidetungstic oxidea zinc oxideindium oxideniobium oxidenickel oxidecobalt oxideand strontium titanate.
[Claim 4]A photoelectric conversion device which has at least a connecting means which connects an electrode of a couple contacted to an electrolyteand an electrode of this couple so that energization is possibleand is characterized by at least one side of an electrode of this couple being the optical semiconductor electrode according to any one of claims 1 to 3.
[Claim 5]It is the photoelectric conversion method of contacting an electrode of a couple mutually connected so that energization was possible to an electrolyteand producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this coupleA photoelectric conversion method that an electrode with which light is irradiated is characterized by being the optical semiconductor

electrode according to any one of claims 1 to 3.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the optical semiconductor electrode to which the specific compound was made to stick on the surface of a metal oxide semiconductorthe photoelectric conversion device using itand the photoelectric conversion method.
[0002]
[Description of the Prior Art]In recent yearsuse of sunlight attracts attention as an energy resource replaced with fossil fuelssuch as petroleum and coal. As a device which transforms light energy into electrical energy directlythe dry type solar cell in which pn junction was formed on inorganic semiconductorssuch as silicon and gallium arsenideis known welland it is put in practical use as a power supply of the object for remote placesor a portable electronic deviceetc. Howeverconversion efficiency with these expensive solar cells is acquired.
On the other handsince the energy and cost which manufacture takes are very highthere is a problem that it is difficult to use as an energy resource.

[0003]The wet solar cell whichon the other handused the photoelectrochemical reaction which occurs by the interface of a semiconductor and an electrolytic solution as an option which transforms light energy into electrical energy is known. As compared with the above-mentioned silicongallium arsenideetc.metal oxide semiconductors used heresuch as titanium oxidetin oxideand a zinc oxidecan be manufactured at far low energy and costand are expected as a future energy conversion material. Howeversince a stable metal oxide semiconductor like titanium oxide has the band gap as large as not less than 3 eVonly about 4% of ultraviolet radiation of sunlight can be usedandthe way things standhigh conversion efficiency cannot be expected. On the surface of these metal oxide semiconductorsas sensitizing dye Thencyanine dye and a xanthene dyeorganic coloring matter (H. -- Tsubomuraet.al.Nature.261and 402 (1976).)such as coumarin coloring matter M. To make Matsumuraet.al.Bull. Chem.Soc. Jpn. 502533 (1977)JP10-92477AJP10-93118Aetc. adsorband to carry out spectral sensitization is

tried. Howeverwhen the above-mentioned cyanine dyea xanthene dyecoumarin coloring matteretc. are usedthere is a problem that photoelectric conversion efficiency is not enough.
[0004]
[Problem(s) to be Solved by the Invention]This invention solves many problems in said formerand makes it a technical problem to attain the following purposes. That isthis invention can carry out available [of the sunlight] efficientlyand is excellent in photoelectric conversion efficiencystabilityenduranceetc. and an object of this invention is to provide the photoelectric conversion device and the photoelectric conversion method of excelling in photoelectric conversion efficiency using the optical semiconductor electrode which can be manufactured cheaply and easilyand this optical semiconductor electrode.
[0005]
[Means for Solving the Problem]Said The means for solving a technical problem is as follows. That isit is an optical semiconductor electrode having a photoelectric conversion layer by at least one sort chosen as the surface of <1> metal oxide semiconductor from a perylene compound expressed with a tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I).
General formula (I)
[0006]
[Formula 12]

[0007]In said general formula (I)R^1 and R^2It may be mutually the sameand may differa hydrogen atoman alkyl groupan aryl groupan aralkyl groupan alkoxyalkyl groupor an acyl group may be expressedand these may form the annular group of the following structure mutually. n expresses 0 or 1.
[0008]
[Formula 13]

[0009]General formula (II)
[Formula 14]

[0010]In said general formula (II)R^3 and R^4Expressing the basis expressed with either following general formula (III) - (IX)these may be mutually the sameit may differ and at least one side expresses the basis

expressed with either following general formula (III) - (VII) and (IX). l expresses 0-12when it is a basis which expresses 0 when R^3 and R^4 are the bases expressed with either following general formula (III) - (VIII)and is expressed with following general formula (IX).
General formula (III)
[0011]
[Formula 15]

[0012]In said general formula (III)R^5 and R^6 may be mutually the sameit may differan aliphatic groupan aromatic groupor a heterocycle group is expressedand these may be replaced by the substituent. A^1 expresses a divalent aliphatic grouparomatic groupor heterocycle groupand these may be replaced by the substituent.
General formula (IV)
[0013]
[Formula 16]

[0014]In said general formula (IV)A^2 expresses a divalent aliphatic grouparomatic groupor heterocycle groupand these may be replaced by the substituent. R^7 and R^8 may be mutually the sameand it may differA hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-20-$(CH_2)_pCOOR^{18}$-$(CH_2)_pSO_3R^{19}$or -$(CH_2)_pR^{20}R^{21}$ is expressed. $R^{18}R^{19}R^{20}$and R^{21} express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.
General formula (V)
[0015]
[Formula 17]

[0016]In said general formula (V)A^3 expresses a single bond or a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by the substituent. R^9 expresses an aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by the substituent. R^{10} A hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-20- (CH_2) Express $_pCOOR^{18}$-$(CH_2)_pSO_3R^{19}$or -$(CH_2)_pNR^{20}R^{21}$. $R^{18}R^{19}R^{20}$and R^{21} express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.
General formula (VI)
[0017]

[Formula 18]

[0018]In said general formula (VI)A^4 expresses a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. X expresses an oxygen atoma sulfur atomor $>NR^{22}$. R^{11} and R^{12} A hydrogen atoma halogen atoman alkyl group of the carbon numbers 1-20- (CH_2) Express $_pCOOR^{18}$-(CH_2) $_pSO_3R^{19}$or -(CH_2) $_pNR^{20}R^{21}$. $R^{18}R^{19}R^{20}R^{21}$and R^{22} express an alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses an integer of 0-20.
General formula (VII)
[0019]
[Formula 19]

[0020]In said general formula (VII)A^5 expresses a single bond or a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. R^{13} expresses a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. R^{14} A hydrogen atoma halogen atoman alkyl group of the carbon numbers 1-20- (CH_2) Express $_pCOOR^{18}$-(CH_2) $_pSO_3R^{19}$or -(CH_2) $_pNR^{20}R^{21}$. $R^{18}R^{19}R^{20}$and R^{21} express an alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses an integer of 0-20.
General formula (VIII)
[0021]
[Formula 20]

[0022]In said general formula (VIII)A^6 expresses a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. Y expresses -COOH-SOOHor $-NH_2$.
General formula (IX)
[0023]
[Formula 21]

[0024]In said general formula (IX)X expresses two hydrogen atoms or MgZnFeConickelCuRuSnSnOTiOVOaluminum (OH)Ga (OH)or In (OH). $R^{15}R^{16}$and R^{17} express a hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-12-(CH_2) $_mCOOH$or -(CH_2) $_mNH_2$. m and n express the integer of 0-12.

<2> A tetracyano anthra quinodimethane compound expressed with said general formula (I) is an optical semiconductor electrode given in the above <1> which is a tetracyano anthra quinodimethane compound expressed with a following general formula (I-a).
General formula (I-a)
[0025]
[Formula 22]

[0026]In said general formula (I-a)Me expresses a methyl group. n expresses 0 or 1.
<3> metal oxide semiconductors are optical semiconductor electrodes given in the above <1> or <2> which is at least one sort chosen from titanium oxidethe tin oxidetungstic oxidea zinc oxideindium oxideniobium oxidenickel oxidecobalt oxideand strontium titanate.
It has at least a connecting means which connects the electrode of the couple contacted to <4> electrolytesand the electrode of this couple so that energization is possibleand at least one side of the electrode of this couple is a photoelectric conversion device characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <3>.
<5> An electrode of a couple mutually connected so that energization was possible is contacted to an electrolyteBy irradiating at least one side of an electrode of this coupleit is the photoelectric conversion method of producing a photoelectric conversion reactionand an electrode with which light is irradiated is the photoelectric conversion method characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <3>.
[0027]
[Embodiment of the Invention](Optical semiconductor electrode) The optical semiconductor electrode of this invention has a photoelectric conversion layer by at least one sort chosen from the perylene compound expressed with the tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I) on the surface of a metal oxide semiconductor.
[0028]- metal oxide semiconductor - As said metal oxide semiconductorthere is no restriction in particularand it can choose suitably according to the purposefor exampletitanium oxidetin oxidetungstic oxidea zinc oxideindium oxideniobium oxidestrontium titanateetc. are mentioned. These may be used by an one-sort independent and may use two or more sorts together. Especially in this inventionthe

reasons of a photoelectric transfer characteristicchemical stabilitymanufacture easeetc. to titanium oxide is preferred also in these.

[0029]About the shape of said metal oxide semiconductorstructureand a sizethere is no restriction in particular and it can choose suitably according to the purpose. For exampleas a structure of said metal oxide semiconductorIt may be the structure which consists only of this metal oxide semiconductorand may be the structure in which the thin film layer of this metal oxide semiconductor was formed on conductive base materialssuch as platessuch as transparent electrodessuch as ITO glass and Nesa glassplatinumcopperand black leador a mesh electrode.

[0030]- photoelectric conversion layer - The surface of said metal oxide semiconductor is adsorbed in at least one sort chosen from the perylene compound expressed with the tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I)and said photoelectric conversion layer is formed in it.

General formula (I)

[0031]

[Formula 23]

[0032]In said general formula (I)R^1 and R^2It may be mutually the sameand may differa hydrogen atoman alkyl groupan aryl groupan aralkyl groupan alkoxyalkyl groupor an acyl group may be expressedand these may form the annular group of the following structure mutually. n expresses 0 or 1.

[0033]

[Formula 24]

General formula (II)

[Formula 25]

[0034]In said general formula (II)R^3 and R^4Expressing the basis expressed with either following general formula (III) - (IX)these may be mutually the sameit may differ and at least one side expresses the basis expressed with either following general formula (III) - (VII) and (IX). l expresses 0-when it is a basis which expresses 0 when R^3 and R^4 are the bases expressed with either following general formula (III) - (VIII)and is expressed with following general formula (IX).

General formula (III)
[0035]
[Formula 26]

[0036]In said general formula (III)R^5 and R^6 may be mutually the sameit may differan aliphatic groupan aromatic groupor a heterocycle group is expressedand these may be replaced by a substituent. A^1 expresses a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent.
General formula (IV)
[0037]
[Formula 27]

[0038]In said general formula (IV)A^2 expresses a divalent aliphatic grouparomatic groupor heterocycle groupand these may be replaced by the substituent. R^7 and R^8 may be mutually the sameand it may differA hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-20-$(CH_2)_pCOOR^{18}$-$(CH_2)_pSO_3R^{19}$or -$(CH_2)_pNR^{20}R^{21}$ is expressed. $R^{18}R^{19}R^{20}$and R^{21} express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.
General formula (V)
[0039]
[Formula 28]

[0040]In said general formula (V)A^3 expresses a single bond or a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by the substituent. R^9 expresses an aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by the substituent. R^{10} A hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-20- (CH_2) Express $_pCOOR^{18}$-$(CH_2)_pSO_3R^{19}$or -$(CH_2)_pNR^{20}R^{21}$. $R^{18}R^{19}R^{20}$and R^{21} express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.
General formula (VI)
[0041]
[Formula 29]

[0042]In said general formula (VI)A^4 expresses a divalent aliphatic

grouparomatic groupor heterocycle groupand these may be replaced by the substituent. X expresses an oxygen atoma sulfur atomor >NR^{22}. R^{11} and R^{12} A hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-20-(CH_2) Express $_pCOOR^{18}$-(CH_2) $_pSO_3R^{19}$or -(CH_2) $_pNR^{20}R^{21}$. $R^{18}R^{19}R^{20}R^{21}$and R^{22} express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.

General formula (VII)

[0043]

[Formula 30]

[0044]In said general formula (VII)A^5 expresses a single bond or a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. R^{13} expresses a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. R^{14} A hydrogen atoma halogen atoman alkyl group of the carbon numbers 1-20- (CH_2) Express $_pCOOR^{18}$-(CH_2) $_pSO_3R^{19}$or -(CH_2) $_pNR^{20}R^{21}$. $R^{18}R^{19}R^{20}$and R^{21} express an alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses an integer of 0-20.

General formula (VIII)

[0045]

[Formula 31]

[0046]In said general formula (VIII)A^6 expresses a divalent aliphatic grouparomatic groupor heterocycle groupand these may be replaced by the substituent. Y expresses -COOH-SOOHor -NH_2.

General formula (IX)

[0047]

[Formula 32]

[0048]In said general formula (IX)X expresses two hydrogen atoms or MgZnFeConickelCuRuSnSnOTiOVOaluminum (OH)Ga (OH)or In (OH). $R^{15}R^{16}$and R^{17} express a hydrogen atoma halogen atomthe alkyl group of the carbon numbers 1-12-(CH_2) $_mCOOH$or -(CH_2) $_mNH_2$. m and n express the integer of 0-12.

[0049]As a desirable example of a tetracyano anthra quinodimethane compound expressed with said general formula (I)the following compound (I-1-30) is mentioned. The example in n= 0 was shown in Table 1and the example in n= 1 was shown in Table 2.

[0050]
[Table 1]

[0051]
[Table 2]

[0052]In this inventionespecially a tetracyano anthra quinodimethane compound that are pointssuch as photoelectric conversion efficiencyan absorption wavelength regionand an ease of manufactureand is expressed with a following general formula (I-a) also in these is preferred (compound expressed with said illustration compound (I-1)).
General formula (I-a)
[0053]
[Formula 33]

In said general formula (I-a)Me expresses a methyl group. n expresses 0 or 1.
[0054]A tetracyano anthra quinodimethane compound expressed with said general formula (I)For exampleit is compoundable by method to which the Anthraquinone derivative expressed with a following general formula (A) of a statement to JP63-104062A and malononitrile expressed with a following general formula (B) are made to reactor a method given in JP58-55450A etc.
[0055]
[Formula 34]

[0056]
[Formula 35]

[0057]Efficientlyseparation and since it is movablethe tetracyano anthra quinodimethane compound expressed with said general formula (I) is efficientand can carry out spectral sensitization of the electric charge which it had an electronic receptiveness portion and an electron-donative portionand the absorption wavelength region is extended to the long wavelength region which is about 700 nmand was generated.
[0058]The following compound (II-1 - 13) is mentioned as a desirable

example of a perylene compound expressed with said general formula (II).

[0059]
[Formula 36]

[0060]
[Formula 37]

[0061]
[Formula 38]

[0062]
[Formula 39]

[0063]
[Formula 40]

[0064]
[Formula 41]

[0065]
[Formula 42]

[0066]
[Formula 43]

[0067]
[Formula 44]

[0068]
[Formula 45]

[0069]
[Formula 46]

[0070]
[Formula 47]

[0071]
[Formula 48]

[0072]In this inventiona following general formula (IX-a) is held as a perylene compound expressed with said general formula (II).
General formula (IX-a)
[0073]
[Formula 49]

[0074]As a desirable example of a perylene compound expressed with said general formula (IX-a)the compound (IX-1 - 23) shown in Table 3 is mentioned.
[0075]
[Table 3]

In Table 3H2expresses two hydrogen atoms.
[0076]In the perylene compound which is said general formula (II) and is expressedR^3 and R^4 are the sameWhat is a basis expressed with either said general formula (III) - (IX)respectively is compoundable byfor examplemaking a 34910-perylene tetracarboxylic anhydride and the compound expressed with following general formula (III') - (IX')respectively react.
[0077]
[Formula 50]

[0078]
[Formula 51]

[0079]
[Formula 52]

[0080]
[Formula 53]

[0081]
[Formula 54]

[0082]
[Formula 55]

[0083]
[Formula 56]

[0084]In a perylene compound which is said general formula (II) and is expressedR^3 differs from R^4 mutuallyWhat is a basis expressed with either said general formula (III) - (IX)For exampleby making two sorts chosen from a 34910-perylene tetracarboxylic anhydride and a compound expressed with said general formula (III') - (IX') reactOr it is compoundable by making two sorts chosen from a compound expressed with 34910-perylene tetracarboxylic monoanhydride mono- metal salt and said general formula (III') - (IX') of a statement by United States patent $_{4th}$the No. $_{501}$ or 906 specificationetc. react one by one.
[0085]A perylene compound expressed with said general formula (II) is excellent in chemical stability and enduranceand is excellent in holdout in the surface of said metal oxide semiconductorand spectral sensitization can be carried out stably and efficient over a long period of time.
[0086]Formation of - photoelectric conversion layer - Said photoelectric conversion layer adds to a solvent at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound expressed with said general formula (I)and said (II)It can form in the surface of this metal oxide semiconductor easily by immersing said metal oxide semiconductor into a solution which dissolved this.
[0087]As said solventprofitablythere is no restriction and it can choose

from publicly known solvents suitably according to the purposeFor exampleamide system solventssuch as ketone solventsuch as alcoholic solventsuch as methanol and isopropyl alcoholacetoneand methyl ethyl ketoneN. N-dimethylformamideand N-methyl pyrrolidonewateror these mixed solvents are mentioned. These may be used by an one-sort independent and may use two or more sorts together. Also in theseamide system solventssuch as N. N-dimethylformamideare preferred. In this inventionit is the purpose of raising solubility to said at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound expressed with said general formula (I)and said (II) of solventsand acidan alkalietc. may be added in this solvent.

[0088]In order to promote adsorption to said at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound which may perform said immersion at a room temperature and is expressed with said general formula (I)and said (II) of metal oxide semiconductorsit may heat if needed.

[0089]After washing after said immersion using arbitrary solvents etc. by carrying out desiccation etc. An optical semiconductor electrode which has the photoelectric conversion layer by which at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound expressed with said general formula (I) and said (II) was adsorbed and formed in the surface of said metal oxide semiconductor is obtained.

[0090]In a wide range of fieldsa semiconductor electrode of this invention can be used conveniently and can be used especially conveniently for the following photoelectric conversion devices and photoelectric conversion methods of this invention.

[0091](Photoelectric conversion device) A photoelectric conversion device of this invention may have at least a connecting means which connects an electrode of a couple contacted to an electrolyteand an electrode of this couple so that energization is possibleand also may have a means of others suitably selected if needed.

[0092]Also in an electrode of said coupleit is an optical semiconductor electrode of said this inventionand another side is a counterelectrode. As said counterelectrodeto oxidation and reductionif stablethere will be no restriction in particularand according to the purposeit can choose from a publicly known thing suitablyfor exampletransparent electrodessuch as platessuch as platinumgoldand black leadITO glassand Nesa glassetc. are mentioned.

[0093]A wire roda platea printed filmor a vacuum evaporation film etc. which restriction in particular does not have as long as it has a

function in which an electrode of said couple can be connected as said connecting means so that energization is possibleand consists of conductive materialssuch as a publicly known lead or various metalcarbonand a metallic oxideis mentioned. This connecting means is connected to an electrode of said couple so that energization is possible.

[0094]As said electrolytethere is no restriction in particular and it can choose suitably according to the purposeFor examplesaltssuch as potassium chloridea lithium chlorideand tetraethylammonium perchlorateNonaqueous solvent solutionssuch as acidssuch as alkalisuch as sodium hydroxide and potassium carbonatesulfuric acidand chloridethese mixturesthese solution or these alcoholand propylene carbonateetc. are mentioned. In this inventionit is the purposessuch as attaining stabilization of the photoelectric current characteristicand a redox reagent which produces an oxidation-reduction reaction still more nearly reversibly [such as potassium iodide iodineand p-benzoquinone] in said electrolyte may be added. A photoelectric conversion device of this invention can be used conveniently for a photoelectric conversion method of the following this inventions.

[0095](A photoelectric conversion method) In a photoelectric conversion method of this inventionan electrode of said couple mutually connected so that energization was possible is contacted to said electrolyteand a photoelectric conversion reaction is produced by irradiating at least one side of an electrode of this couple. [0096]In an electrode of said couplean electrode with which light is irradiated is an optical semiconductor electrode of said this inventionand another side is said counterelectrode.

[0097]- In a photoelectric conversion device and a photoelectric conversion method of photoelectric conversion reaction-this inventiona photoelectric conversion reaction arises as follows. That issaid optical semiconductor electrode and said counterelectrode are first immersed into said electrolyte (solution). Nextmonochromatic light of at least one sort of absorption wavelength regions chosen as said optical semiconductor electrode from a perylene compound expressed with a tetracyano anthra quinodimethane compound expressed with said general formula (I)and said general formula (II)Or an exposure of white light or multicolor light which includes one of the zones will transform such light energies into electrical energy.

[0098]According to a photoelectric conversion device and a photoelectric conversion method using a semiconductor electrode and this semiconductor electrode of this invention. Even if it irradiates with 300-700-nm

visible light as a light with which it irradiates especiallygood photoelectric conversion efficiency is acquiredmetal oxide semiconductorssuch as titanium oxide-- if independentit can use effectively to a wavelength band of visible light which cannot be usedand luminous energiessuch as sunlightcan be efficiently transformed into electrical energy.

[0099]

[Example]Hereafteralthough the example of this invention is describedthis invention is not limited to these examples at all.

[0100](Example 1) 25 ml of alt. titanic acid tetraisopropyl was added graduallyagitating violently in the mixed solution of 150 ml of pure waterand the concentrated nitric acid 1.54g (specific gravity: 1.38). Temperature up was carried out to 80 **continuing churning furthermorechurning was continued at the temperature for 8 hoursand the milky stable titanium oxide colloidal solution was prepared. This titanium oxide colloidal solution was condensed to 40 ml at 30 ** under decompression of 30mmHg. Said titanium oxide colloidal solution was coated with the spin coat method on the glass substrate (the following "ITO glass substrate" is called) with which the layer of ITO was coveredand was calcinated at 500 ** for 1 hour. This operation was repeated 3 times and the titanium oxide layer about 1.0 micrometer thick was formed on the ITO glass substrate. When the crystal structure of the obtained titanium oxide membrane was checked with the X-ray diffraction methodit was a mixture of an anatase and a rutile type. The ITO glass substrate which supported said titanium oxide layer was used as a metal oxide semiconductor.

[0101]After making the solution which dissolved in 50 ml of N.N-dimethylformamide immerse 100 mg of said illustration compound (I-1) at about 90 ** for 12 hoursthis metal oxide semiconductor was washed in order of acetone and methanoland natural seasoning was carried out. By the aboveadsorption formation of the photoelectric conversion layer with said illustration compound (I-1) was carried out on the surface of said metallic-oxide N semiconductor.

[0102]Nextthe lead was connected to the layer portion of ITO covered by the glass substrate. The terminal area of said lead covered and adhered with the epoxy resin. The optical semiconductor electrode was produced by the above.

[0103]Drawing 1 is an approximate account figure for explaining the produced optical semiconductor electrode. The optical semiconductor electrode 1 has the layer 3 of ITOthe titanium oxide layer 4and the photoelectric conversion layer 5 with said illustration compound (I-1)

on the glass base material 2 at this order. The terminal area of the layer 3 of ITO and the lead 7 was covered with the epoxy resin as the adhesive agent 6and has adhered with it.
In this terminal areathe lead 7 is accommodated into the glass tube 8.

[0104]Drawing 2 is an approximate account figure for explaining the photoelectric conversion method using the photoelectric conversion device provided with said optical semiconductor electrode. Heresaturated calomel electrode ** is immersed in a platinum electrode as the optical semiconductor electrode 1 and the counterelectrode 9 which were producedand is immersed into the inside of the transparent glass cell 13and the electrolytic solution 11 as the reference electrode 10. The electrolytic solutions 11 are 0.1M-sodium sulfate / 0.02M-potassium iodide solution. It is connected to the potentiostat 12 via the lead 7 as a connecting meansand energization of each electrode is attained.
[0105]In this photoelectric conversion deviceit held so that the potential of said optical semiconductor electrode 1 might be set to 0V to the reference electrode 10and it irradiated with white light (the xenon lamp of 500Willumination 4000lux) from the back side of the optical semiconductor electrodeand the value of the photoelectric current at this time was measured with the potentiostat. The measurement result was shown in Table 4.
[0106](Example 2) In Example 1the outside which replaced the illustration compound (I-1) with the illustration compound (I-3) produced the optical semiconductor electrode and the photoelectric conversion device like Example 1enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 4.
[0107](Example 3) In Example 1the outside which replaced the illustration compound (I-1) with the illustration compound (I-7) produced the optical semiconductor electrode and the photoelectric conversion device like Example 1enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 4.
[0108](Comparative example 1) In Example 1the outside which did not use an illustration compound (I-1) produced the optical semiconductor electrode and the photoelectric conversion device like Example 1enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 4.
[0109](Comparative example 2) The outside which replaced the illustration compound (I-1) with 2457-tetraiodofluorescein in Example 1

is an example. The optical semiconductor electrode and the photoelectric conversion device were produced like 1the photoelectric conversion method was enforcedand photoelectric current was measured. The measurement result was shown in Table 4.

[0110](Comparative example 3) The outside which replaced the illustration compound (I-1) with copper (tetra KARUBOKI phthalocyaninato) (II) in Example 1 is an example. The optical semiconductor electrode and the photoelectric conversion device were produced like 1the photoelectric conversion method was enforcedand photoelectric current was measured. The measurement result was shown in Table 4.

[0111]

[Table 4]

[0112](Example 4) In Example 1a metal oxide semiconductor instead of making the solution which dissolved in 50 ml of N.N-dimethylformamide immerse 100 mg of said illustration compound (I-1) at about 90 ** for 12 hoursThe outside in which the solution which dissolved in 50 ml of 2% hydroxylation tetra (n-butyl) ammonium / ethanol solutions was made to immerse 50 mg of an illustration compound (II-4) at 70-80 ** for 1 hour produces an optical semiconductor electrode and a photoelectric conversion device like Example 1and the photoelectric conversion method is enforcedPhotoelectric current was measured. The measurement result was shown in Table 5.

[0113](Example 5) In Example 4the outside which replaced the illustration compound (II-4) with the illustration compound (II-9) produced the optical semiconductor electrode and the photoelectric conversion device like Example 4enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 5.

[0114](Example 6) In Example 4the outside which replaced the illustration compound (II-4) with the illustration compound (II-10) produced the optical semiconductor electrode and the photoelectric conversion device like Example 4enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 5.

[0115](Comparative example 4) In Example 4the outside which did not use an illustration compound (II-4) produced the optical semiconductor electrode and the photoelectric conversion device like Example 4enforced the photoelectric conversion methodand measured photoelectric current.

The measurement result was shown in Table 5.
[0116](Comparative example 5) In Example 4the outside which replaced the illustration compound (II-4) with 2457-tetraiodofluorescein produced the optical semiconductor electrode and the photoelectric conversion device like Example 4enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 5.
[0117]
[Table 5]

[0118](Example 7) In Example 1a metal oxide semiconductor instead of making the solution which dissolved in 50 ml of N.N-dimethylformamide immerse 100 mg of said illustration compound (I-1) at about 90 ** for 12 hoursThe outside in which the solution which dissolved in 50 ml of N.N-dimethylformamide was made to immerse 100 mg of an illustration compound (IX-4) at 80-100 ** for 1 hour produced the optical semiconductor electrode and the photoelectric conversion device like Example 1enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 6.
[0119](Example 8) In Example 7the outside which replaced the illustration compound (IX-4) with the illustration compound (IX-7) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 6.
[0120](Example 9) In Example 7the outside which replaced the illustration compound (IX-4) with the illustration compound (IX-9) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 6.
[0121](Comparative example 6) In Example 7the outside which did not use an illustration compound (IX-4) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 6.
[0122](Comparative example 7) In Example 7the outside which replaced the illustration compound (IX-4) with 2457-tetraiodo-3'4'5'6'-tetrachlorofluoresceinThe optical semiconductor electrode and the photoelectric conversion device were produced like Example 7the photoelectric conversion method was enforcedand photoelectric current

was measured. The measurement result was shown in Table 6.
[0123](Comparative example 8) In Example 7the outside which replaced the illustration compound (IX-4) with copper (tetracarboxy phthalocyaninato) (II) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 6.
[0124]
[Table 6]

[0125]
[Effect of the Invention]According to this inventionavailable [of the sunlight] can be carried out efficientlyit excels in photoelectric conversion efficiencystabilityenduranceetc. and the photoelectric conversion device and the photoelectric conversion method of excelling in photoelectric conversion efficiency can be provided using the optical semiconductor electrode which can be manufactured cheaply and easilyand this optical semiconductor electrode.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]Drawing 1 is an approximate account figure of the optical semiconductor electrode of this invention.
[Drawing 2]Drawing 2 is an approximate account figure for explaining the photoelectric conversion method using the photoelectric conversion device provided with the optical semiconductor electrode of drawing 1.
[Drawing 3]Drawing 3 is an ultraviolet and visible absorption spectrum of the optical semiconductor electrode of Example 4.
[Drawing 4]Drawing 4 is an ultraviolet and visible absorption spectrum of the optical semiconductor electrode of Example 7.
[Description of Notations]
1 Optical semiconductor electrode
2 Glass substrate
3 The layer of ITO
4 Titanium oxide layer
5 Photoelectric conversion layer
6 Adhesive agent
7 Lead

8 Glass tube
9 Counterelectrode
10 Reference electrode
11 Electrolytic solution
12 Potentiostat
13 Transparent glass cell